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04. Equilibrium Thermodynamics IV: Applications

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Abstract

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[tex14] Entropy and internal energy of the classical ideal gas

The classical ideal gas for a fixed number N of particles is specified by the equation of state $pV = Nk_B T$ and the constant heat capacity $C_V = \alpha Nk_B$ [$\alpha = \frac{3}{2}$ (monatomic), $\alpha = \frac{5}{2}$ (diatomic), $\alpha = 3$ (polyatomic)].

(a) Use this information to calculate the internal energy $U(T, V)$ and show that the result is, in fact, independent of V . Use the same information to calculate the entropy $S(T, V)$. Introduce reference values T_0, V_0, U_0, S_0 for the integrations.

(b) Determine the mechanical response functions α_p (thermal expansivity), κ_T (isothermal compressibility), and κ_S (adiabatic compressibility).

Solution:

[tex15] Thermodynamic potentials of the classical ideal gas

The classical ideal gas for a fixed number N of particles is specified by the equation of state $pV = Nk_B T$ and the constant heat capacity $C_V = \alpha Nk_B$ [$\alpha = \frac{3}{2}$ (monatomic), $\alpha = \frac{5}{2}$ (diatomic), $\alpha = 3$ (polyatomic)]. From the functions $U(T)$ and $S(T, V)$ determined in [tex14] calculate the thermodynamic potentials $U(S, V)$ (internal energy), $E(S, p)$ (enthalpy), $A(T, V)$ (Helmholtz potential) and $G(T, p)$ (Gibbs potential). Use the reference values T_0, V_0, U_0, S_0 from [tex14].

Solution:

[tex17] Chemical potential of the classical ideal gas

Calculate the chemical potential $\mu(T, p)$ of the classical ideal gas by integrating the Gibbs-Duhem equation, $SdT - Vdp + Nd\mu = 0$, with $V(T, p)$ from the equation of state and $S(T, p)$ from [tex14]. Compare the result with the Gibbs free energy per particle, $G/N = \mu$, calculated in [tex15].

Solution:

[tex35] Ideal gas heat capacity by design

Consider 1mol of a classical ideal gas [$pV = RT, C_V = \frac{3}{2}R$].

(a) If C_X is the heat capacity of a reversible process in which the thermodynamic variable X is kept constant, show that this process is described by a curve $pV^f = \text{const}$ in the (p, V) -plane with $f = (C_p - C_X)/(C_X - C_V)$.

(b) Discuss the result for three special cases: $X = p$, $X = V$, $X = S$.

Solution:

[tex18] Sound velocity in the classical ideal gas I

In a sound wave the classical ideal gas [$pV = nRT$, $C_V = \alpha nR = \text{const}$, molar mass M] is *adiabatically* compressed and expanded.

(a) Show that the sound velocity is related to the adiabatic compressibility κ_S and the mass density ρ as follows:

$$c^2 = \frac{1}{\rho \kappa_S} = \left(\frac{\partial p}{\partial \rho} \right)_S.$$

(b) Use thermodynamic properties of the classical ideal gas to infer from this expression the result $c^2 = \gamma RT/M$, where $\gamma = 1 + 1/\alpha$.

Solution:

[tex99] Sound velocity in the classical ideal gas II

Show that the internal energy per unit mass and the enthalpy per unit mass of a classical ideal gas with heat capacity $C_V = \text{const}$ can be expressed as follows in terms of the sound velocity $c = \sqrt{(\partial p / \partial \rho)_S}$ and the ratio of heat capacities $\gamma = C_p / C_V$:

$$\bar{U} = \bar{U}_0 + \frac{c^2}{\gamma(\gamma - 1)}, \quad \bar{E} = \bar{U}_0 + \frac{c^2}{\gamma - 1},$$

where \bar{U}_0 is a constant.

Solution:

[tex134] **Absolute temperature from measurements**

Consider a compressible fluid in an insulating cylinder with a movable piston, a calibrated heat source, a pressure gauge, and a thermometer with arbitrary temperature scale θ . The experiment consists of measurements over a range of θ of the following quantities:

- rate $A(\theta) = (\delta V / \delta \theta)_p$ at which volume increases during isobaric heating up,
- rate $B(\theta) = (\delta Q / \delta p)_\theta$ at which heat is supplied during isothermal decompression.

Show that from the data of these two experiments we can infer the following differential relation between the thermometer reading θ and the absolute temperature T :

$$\frac{d \ln T}{d \theta} = -\frac{A(\theta)}{B(\theta)}.$$

The (undetermined) integration constant of $\ln T(\theta)$ can be used to fix the scale of the absolute temperature (e.g. by using the triple point of H_2O).

Solution:

[tex138] Polytropic process of classical ideal gas

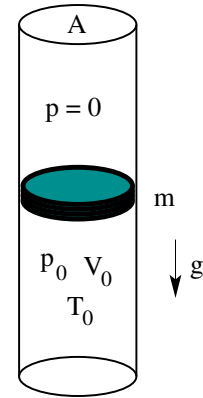
Consider an ideal monatomic gas [$pV = Nk_B T, C_V = \frac{3}{2}Nk_B$] confined to a cylinder by a movable piston. The gas is compressed from volume V_1 to volume $V_2 < V_1$ under circumstances such that the relation $pV^x = a$ with $a = \text{const}$ is satisfied. In this polytropic process, determine the quantities ΔW (work done on the system), ΔU (change in internal energy), and ΔQ (heat added to the system) as functions of V_1 and V_2 . Determine for which values of x ($0 < x < 2$) each of these quantities is positive or negative.

Solution:

[tex141] Heavy piston

A cylinder of cross section A with insulating walls has two compartments separated by a disk of mass m . The axis of the cylinder is vertical. A uniform gravitational field g is present. The disk is initially held at a fixed position by an external agent. The upper compartment is evacuated and the lower compartment contains 1 mol of a monatomic, classical, ideal gas [$pV = RT$, $C_V = \frac{3}{2}R$] at temperature T_0 , volume V_0 , and pressure p_0 . When the disk is released, it moves without (wall) friction and comes to rest at a lower position. Calculate the final values p_1, V_1, T_1 of pressure, volume, and temperature, respectively. The disk does not exchange heat. The only significant action of the gravitational field is on the disk.

Hint: Use energy conservation and Newton's third law. Assume thermal equilibrium for the initial and final states.



Solution:

[tex150] Isothermal atmosphere

Consider a column of air [molar mass $M = 29\text{g}$] treated as a classical ideal gas [$pV = nRT$] in a uniform gravitational field $g = 9.81\text{m/s}^2$. The column is assumed to be in thermal equilibrium.

(a) Calculate the dependence of pressure p on height z and (uniform) temperature T , assuming that the pressure is p_0 at $z = 0$.

(b) At what height z_1 (in meters) has the pressure fallen to half of p_0 and at what height z_2 to one percent of p_0 if the temperature is 20°C everywhere?

Hint: Start from the relation, $dp(z) = -\rho(z)d\mathcal{U}(z)$, between pressure p , mass density ρ , and gravitational potential \mathcal{U} at height z . This relation expresses the increment of pressure caused by the weight of a thin layer of air. The ideal-gas equation of state is assumed to hold locally at all heights.

Solution:

[tex151] Adiabatic atmosphere

Consider a column of air [molar mass $M = 29\text{g}$] treated as a classical ideal gas [$pV = nRT$, $C_p/C_V = \gamma = 1.41$] in a uniform gravitational field $g = 9.81\text{m/s}^2$. The column is assumed to be in mechanical equilibrium but not (yet) in thermal equilibrium. The mechanical equilibrium is established by gravitational pressure and governed by the adiabatic relation $pV^\gamma = \text{const}$.

(a) Calculate the dependence on height z of the pressure p , the mass density ρ , and the temperature T , assuming that $p = p_0$ and $T = T_0$ at $z = 0$.

(b) Find the height z_m , expressed as a function of T_0 , at which T , p , and ρ all reach zero. What is that height (in meters) if T_0 is room temperature?

Hints: (i) Infer from $pV^\gamma = \text{const}$ the differential relation $dT/T = [(\gamma - 1)/\gamma]dp/p$. (ii) Use the relation $dp(z) = -\rho(z)d\mathcal{U}(z)$ from [tex150] linking pressure, mass density, and gravitational potential to infer differential equations for $T(z)$ and $p(z)$.

Solution:

[tex152] Homogeneous atmosphere

Meteorological modeling uses the concept of homogeneous atmosphere with constant density over some vertical distance. Consider a column of air [molar mass $M = 29\text{g}$] treated as a classical ideal gas [$pV = nRT$] in a uniform gravitational field $g = 9.81\text{m/s}^2$. The column is assumed to have constant mass density $\rho(z) = \rho_0 = \text{const.}$

- (a) Calculate the dependence on height z of the pressure p and the temperature T , assuming that $p = p_0$ and $T = T_0$ at $z = 0$.
- (b) Find the height z_h , expressed as a function of T_0 , at which T and p both reach zero.
- (c) What must be the temperature (in $^{\circ}\text{C}$) at sea level so that the homogeneous atmosphere just reaches the tip of Mount Everest?

Hints can be gleaned from [tex150] and [tex151].

Solution:

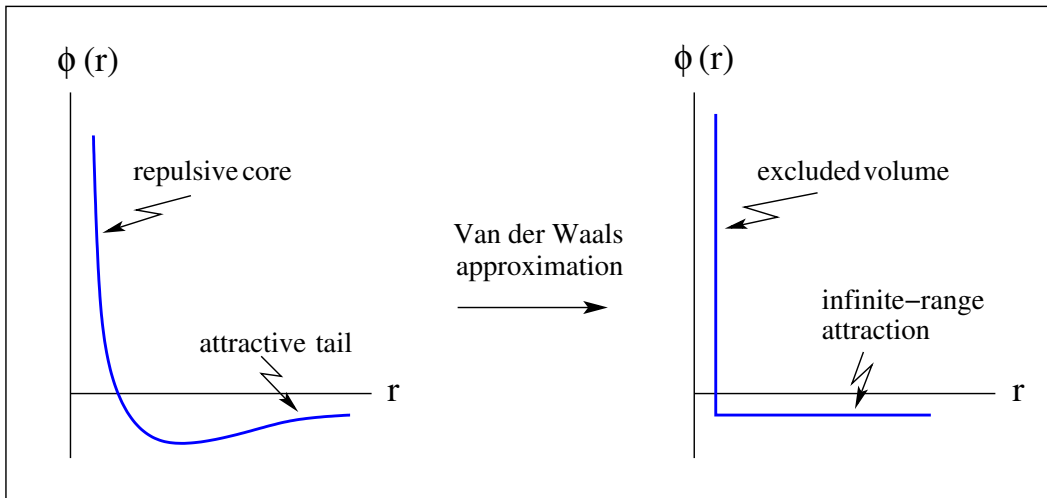
Van der Waals equation of state [tln22]

Atoms of gases interact via short-range force. The ideal gas equation of state, $pV = nRT$, neglects the interaction completely. The van-der Waals equation of state takes it into account summarily:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT,$$

where a, b are empirical parameters.

- nb : excluded volume due to the repulsive core of the interaction at short distances,
- $-an^2/V^2$: pressure correction due to the attractive tail of the interaction at long distances.



Cooling of gases [tln23]

During expansion, a gas does work against attractive intermolecular forces. In the process, the average potential energy increases and, by virtue of energy conservation, the average kinetic energy decreases. The result is a drop in temperature. We discuss two processes to illustrate this effect.

Joule effect: free expansion

Free expansion involves no heat transfer and no work performance:
 $\Delta Q = 0, \Delta U = 0,$

Initial state: V_i, p_i, T_i ; final state: V_f, p_f, T_f with $p_f < p_i$.

The temperature change in the expanding gas is calculated for a quasi-static process between the same equilibrium states.

$$\text{Use } \left(\frac{\partial U}{\partial T}\right)_V = C_V, \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\text{Joule coefficient: } \left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} = \frac{1}{C_V} \left[p - T \left(\frac{\partial p}{\partial T}\right)_V \right].$$

$$\text{Ideal gas: } T \left(\frac{\partial p}{\partial T}\right)_V = p \Rightarrow \text{no effect.}$$

Joule-Thomson effect: throttling

The gas is forced through a porous wall between two chambers. During the process the pressure is constant in both chambers. In the following we consider quasi-static throttling.

Initial state: V_i, p_i, T_i ; final state: V_f, p_f, T_f with $p_f < p_i$.

$$\Delta Q = 0, \Delta U = \Delta W = -\int_0^{V_f} p_f dV - \int_{V_i}^0 p_i dV = -p_f V_f + p_i V_i.$$

$$\Rightarrow U_i + p_i V_i = U_f + p_f V_f = \text{const.} \Rightarrow E = \text{const.} \Rightarrow dE = T dS + V dp = 0.$$

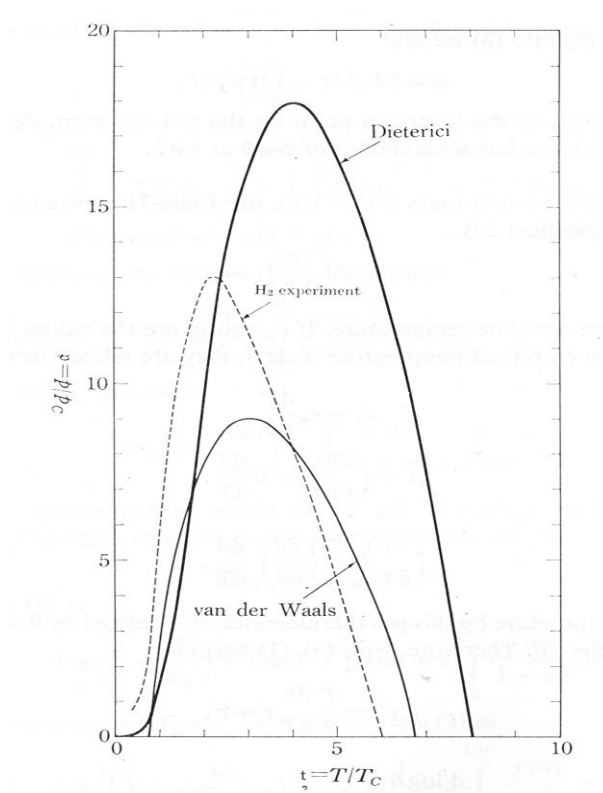
$$\text{Use } \left(\frac{\partial E}{\partial T}\right)_p = C_p, \left(\frac{\partial E}{\partial p}\right)_T = T \left(\frac{\partial S}{\partial p}\right)_T + V = -T \left(\frac{\partial V}{\partial T}\right)_p + V.$$

$$\text{Joule-Thomson coefficient: } \left(\frac{\partial T}{\partial p}\right)_E = -\frac{(\partial E/\partial p)_T}{(\partial E/\partial T)_p} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V \right].$$

$$\text{Ideal gas: } T \left(\frac{\partial V}{\partial T}\right)_p = V \Rightarrow \text{no effect.}$$

Joule–Thomson inversion curves [ts11]

- Hydrogen gas: experimental data.
- Van der Waals gas: $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$.
- Dieterici gas: $p = \frac{nRT}{V - nb} \exp\left(-\frac{an}{RTV}\right)$.



[from Kubo: Thermodynamics]

[tex27] Heat capacities of the van der Waals gas

Consider the van der Waals equation of state for $n = 1$ mol of a gas:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT.$$

- (a) Show that the heat capacity C_V may depend on T but is independent of V .
- (b) Calculate the quantity $C_p - C_V$ as a function of p and V . Verify that $C_p - C_V \rightarrow R$ in the ideal gas limit.

Solution:

[tex38] Internal energy and entropy of van der Waals gas

Calculate the internal energy $U(T, V)$ and the entropy $S(T, V)$ of the van der Waals gas, specified by the equation of state

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T$$

and the specific heat $C_V = \alpha Nk_B$.

Solution:

[tex31] Joule coefficient of van der Waals gas

The cooling of a gas via free expansion is described by the Joule coefficient

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V} \left[p - T \left(\frac{\partial p}{\partial T}\right)_V \right].$$

- (i) Determine the Joule coefficient for 1 mol of the ideal gas [$pV = RT, C_V = \alpha R$] and for 1mol of the van der Waals gas [$(p + a/V^2)(V - b) = RT, C_V = \alpha R$].
(ii) Calculate the temperature change $T_f - T_i$ when the van der Waals gas is freely expanded from V_i to $V_f > V_i$.

Solution:

[tex32] Joule–Thomson coefficient of van der Waals gas

The cooling of a gas via throttling is described by the Joule-Thomson coefficient

$$\left(\frac{\partial T}{\partial p}\right)_E = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V \right].$$

- (i) Determine the Joule-Thomson coefficient for 1 mol of the van der Waals gas $[(p+a/V^2)(V-b) = RT, C_V = \alpha R]$.
- (ii) Throttling results in cooling only if $(\partial T/\partial p)_E > 0$. In the (T, p) -plane, this region is bounded by the inversion curve, which is determined by the condition $(\partial T/\partial p)_E = 0$. Calculate the inversion condition $p^*(T)$ for the van der Waals gas.
- (iii) Throttling is most efficient for cooling if it starts at the highest possible pressure. Find the temperature at which the inversion curve has a maximum.

Solution:

[tex29] Assembling thermodynamic information

The following thermodynamic information is known about $n = 1\text{mol}$ of a system:

- At constant temperature T_0 , the work done on the system when it is compressed from V_0 to V is $\Delta W_0 = -RT_0 \ln(V/V_0)$.
- The entropy is $S(T, V) = R(V_0/V)(T/T_0)^a$, where V_0, T_0, a are constants.

Use this information to determine (i) the Helmholtz free energy $A(T, V)$, (ii) the equation of state $f(p, V, T) = 0$, and (iii) the work of compression ΔW done at an arbitrary temperature T .

Solution:

[tex11] **How not to modify the ideal gas equation of state**

Suppose we know empirically that for a real system with fixed n , the product of the pressure p and the volume V is a function of the temperature alone, $pV = f(T)$, and that the internal energy is also a function of the temperature alone, $U = U(T)$. These properties are realized in the classical ideal gas, where $f(T) = nRT$ and $U(T) = C_V T$ with $C_V = \alpha nR = \text{const}$. Show that the only function $f(T)$ in the equation of state of the above form which is compatible with $U = U(T)$, i.e. with $(\partial U / \partial V)_T = 0$ is linear in T with zero intercept: $f(T) = rT$ with $r = \text{const}$.

Solution:

[tex42] Reconstructing the equation of state of a fluid system

A fluid system is found to have a thermal expansivity $\alpha_p = (nR/pV) + (na/RT^2V)$ and an isothermal compressibility $\kappa_T = (n/V)[Tf(p) + b/p]$, where a, b are constants and $f(p)$ is an unknown function.

- (a) Find the function $f(p)$ which makes the two response functions thermodynamically consistent.
- (b) Reconstruct the equation of state $V = V(T, p)$ from the two response functions.

Solution:

[tex43] Reconstructing the equation of state of a gas

It is found for a gas that $\alpha_p = RV/np + aV/nT^2$ and $\kappa_T = T(V/n)f(p)$, where a is a constant and $f(p)$ is an unknown function.

- (a) Find the function $f(p)$ which makes the two response functions thermodynamically consistent.
- (b) Reconstruct the equation of state $g(V, T, p) = 0$ from the two response functions.

Solution:

[tex33] Effects of first virial correction on ideal gas properties

The ideal gas equation of state supplemented by the first virial correction reads $p = (nRT/V)[1 + (n/V)B(T)]$. The associated heat capacity at constant volume can be written in the form $C_V = \frac{3}{2}nR - (n^2R/V)F(T)$, where $F(T)$ and $B(T)$ are related by thermodynamic consistency conditions.

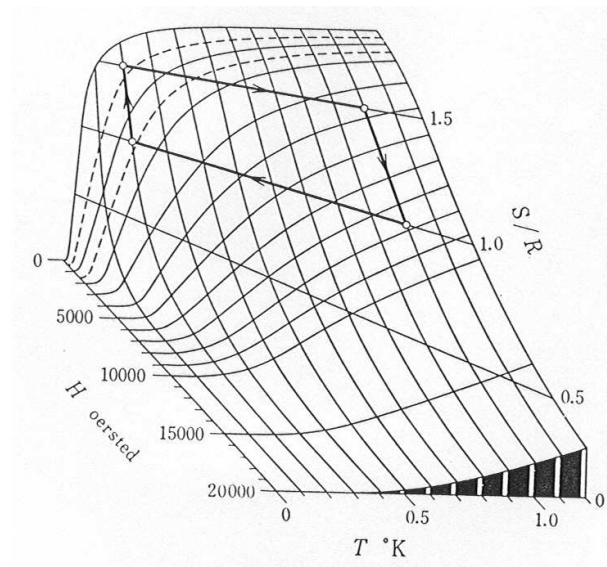
- (a) Express $F(T)$ as a function of $B(T)$.
- (b) Find the function $U(T, V)$ (internal energy) and $S(T, V)$ (entropy) for this system.
- (c) Find the first virial correction $B(T)$ for the van der Waals gas, $[p + a(n/V)^2](V - nb) = nRT$, and calculate the associated virial correction $F(T)$ to the heat capacity C_V .

Solution:

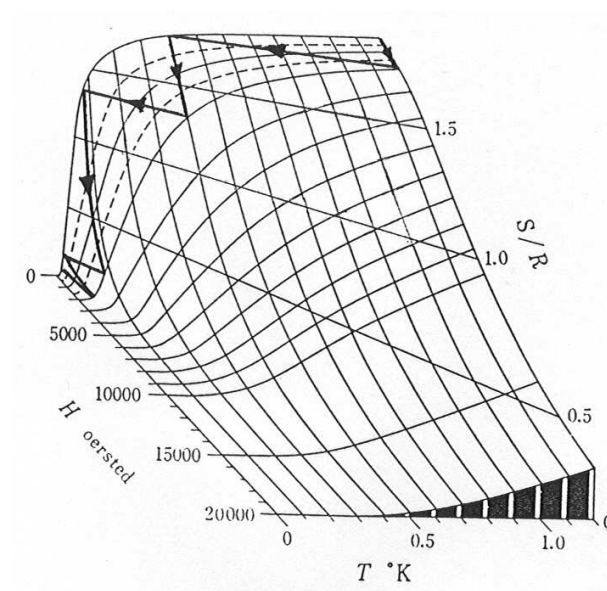
Entropy due to electronic spins in iron ammonium alum [tsl2]

Dependence of entropy on temperature and magnetic field for paramagnet.

(a) Carnot cycle operating on this system.



(b) Cooling of this system via adiabatic demagnetization.



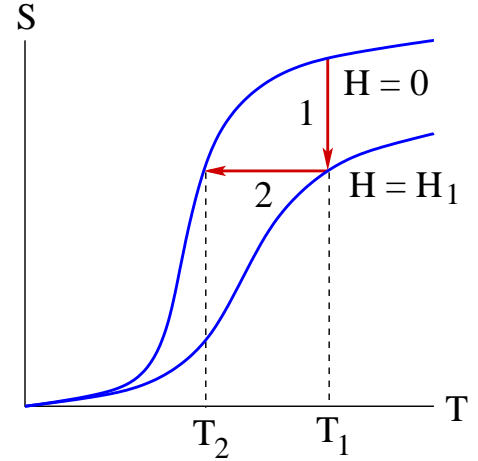
Adiabatic demagnetization [tln24]

Equation of state for paramagnetic salt in a weak magnetic field: $M(T, H) = \chi_T(T)H$.

Helmholtz free energy:

$$dA = -SdT + HdM, \quad \left(\frac{\partial A}{\partial M} \right)_T = H = \frac{M}{\chi_T}$$

$$\Rightarrow A(T, M) = A(T, 0) + \frac{M^2}{2\chi_T}.$$



Entropy: $S(T, M) = - \left(\frac{\partial A}{\partial T} \right)_M = S(T, 0) - \frac{1}{2}M^2 \left[\frac{d}{dT} \chi_T^{-1} \right]$

$$\Rightarrow S(T, H) = S(T, 0) + \frac{1}{2}H^2 \frac{d\chi_T}{dT}; \quad \chi_T > 0, \quad \frac{d\chi_T}{dT} < 0 \text{ for paramagnet.}$$

Third law: $\lim_{T \rightarrow 0} S(T, H) = 0$ independent of $H \Rightarrow \lim_{T \rightarrow 0} \frac{d\chi_T}{dT} = 0$.

1. Isothermal magnetization: $\Delta S = \frac{1}{2} \frac{d\chi_T}{dT} H_1^2 < 0$.

Heat expelled from system: $\Delta Q = T_1 \Delta S$.

2. Adiabatic demagnetization: $\Delta S = 0 \Rightarrow S(T_1, H_1) = S(T_2, 0)$.

$$\Rightarrow S(T_2, 0) = S(T_1, 0) + \frac{1}{2}H_1^2 \frac{d\chi_T}{dT} \Big|_{T_1} \Rightarrow T_2 < T_1.$$

Consider the entropy function $S(T, H)$ for iron ammonium alum.

- The sequence of steps 1 and 2 approaches absolute zero. As $T \rightarrow 0$, adiabates and isotherms become increasingly parallel, implying a diminishing efficiency of the cooling process.
- The sequence of steps requires heat reservoirs at various temperatures. They can be established by employing a Carnot engine consisting of steps 1 and 2 and their inverses.
- Magnetic refrigerators using paramagnetic salts attain $\sim 0.2\text{K}$. Adiabatic demagnetization attains mK temperatures.

[tex19] Thermodynamics of an ideal paramagnet I

For an ideal paramagnet specified by the equation of state $M = H/T$ (Curie law) and internal energy $U = 0$, find (a) the entropy $S(T, H)$, (b) the thermodynamic potentials $E(S, H)$, $A(T, M)$, $G(T, H)$, and (c) the response functions $C_M, C_H, \chi_T, \chi_S, \alpha_H$.

Solution:

[tex20] Thermodynamics of an ideal paramagnet II

For an ideal paramagnet specified by the equation of state $M = H/T$ (Curie law) and heat capacity $C_M = \text{const}$, find (a) the internal energy $U(T, H)$, the entropy $S(T, H)$, and the enthalpy $E(T, H)$; (b) the thermodynamic potentials $A(T, M)$, $G(T, H)$; (c) the response functions χ_T , χ_S , α_H , C_H .

Solution:

[tex21] Thermodynamics of an ideal paramagnet III

For an ideal Langevin paramagnet, which is specified by the equation of state $M = \tanh(H/T)$ (Langevin function) and the internal energy $U \equiv 0$, find (a) the entropy $S(T, H)$ and the enthalpy $E(T, H)$; (b) the thermodynamic potentials $A(T, M)$, $G(T, H)$; (c) the response functions χ_T , χ_S , α_H , C_H . Determine the integration constant S_0 in $S(T, H)$ such that $S \rightarrow 0$ for $T \rightarrow 0$ and $H \neq 0$ in accordance with the third law of thermodynamics.

Solution:

[tex36] Thermodynamics of a real paramagnet

The magnetization M of a paramagnetic system was measured over a certain temperature range, and it was found to depend only on the ratio H/T : $M = f(H/T)$.

- (a) Show that the internal energy is then independent of H : $U = U(T)$.
(b) Show that the entropy then has the following functional form:

$$S(T, H) = S_1(T) - \frac{H}{T} f\left(\frac{H}{T}\right) + \int_0^{H/T} dx f(x), \quad \text{where } S_1(T) = S_0 + \int_{T_0}^T dT' \frac{U'(T')}{T'}.$$

Solution:

[tex22] Thermodynamics of a classical ideal paramagnetic gas I

Consider 1mol of a paramagnetic gas, specified by the equations of state $pV = RT$ (classical ideal gas) and $M = H/T$ (Curie paramagnet), and by a constant heat capacity $C_{VM} = \frac{3}{2}R$.

(a) Calculate the internal energy $U(T, V, M)$ by integration of the differential $dU = TdS - pdV + HdM$. Show that U only depends on T . (b) Calculate the entropy $S(T, V, M)$ by integration of the differential $dS = (1/T)dU + (p/T)dV - (H/T)dM$. (c) Calculate the Helmholtz potentials $A_M(T, V, M) \doteq U - TS$ and $A_H(T, V, H) \doteq U - TS - MH$. (d) Calculate the Gibbs potentials $G_M(T, p, M) \doteq U - TS + pV$ and $G_H(T, p, H) \doteq U - TS + pV - MH$.

Solution:

[tex133] Thermodynamics of a classical ideal paramagnetic gas II

Consider the fixed amount $n = 1\text{mol}$ of a paramagnetic gas, specified by the equations of state $pV = RT$, $M = H/T$, and by the heat capacity $C_{VM} = 3R/2$.

(a) Characterize a general adiabatic process by a functional relation of the form $f(T, p, H) = \text{const.}$ Start from the function $S(T, V, M)$ derived in [tex22].

(b) Show that the heat transfer is path-independent for isothermal processes. Derive an expression for the heat transfer ΔQ_T of a general isothermal process between (p_0, H_0) and p_1, H_1 .

(c) Show that the heat transfer for isobaric processes does depend on the path taken. Derive an expression for the heat transfer ΔQ_p of the isobaric process $(T_0, H_0) \rightarrow (T_0, H_1) \rightarrow (T_1, H_1) \rightarrow (T_1, H_0) \rightarrow (T_0, H_0)$ along straight segments in the (T, H) -plane.

(d) Consider a process $(T, P_0, H_0) \rightarrow (T, P_1, P_1)$ with $p_0 > p_1$ that is both isothermal (no change in energy) and adiabatic (no heat transfer). In this process mechanical work $\Delta W_p(T, p_0, p_1)$ done by the system is matched by the same amount of magnetic work $\Delta W_H(T, H_0, H_1)$ done on the system. Find $\Delta W_p(T, p_0, p_1)$ and $\Delta W_p(T, p_0, p_1)$.

Solution:

[tex132] Hydrostatic pressure

The chemical potential in a homogeneous fluid is a function $\mu = \mu_0(p, T)$ such as calculated in [tex17] for the classical ideal gas. What remains uniform throughout the fluid in the presence of a uniform gravitational field is the potential

$$\mu = \mu_0(p, T) + mgz = \text{const.},$$

where m is the mass of the fluid particle, g is the acceleration due to gravity, and the z -direction is against the field. For a fluid of negligible compressibility derive from the condition $d\mu/dz = 0$ the familiar result for the hydrostatic pressure,

$$p(z) = p_0 - \rho gz,$$

where $\rho = Nm/V$ is the (average) mass density of the fluid.

Solution:

[tex39] Rubber band heat engine

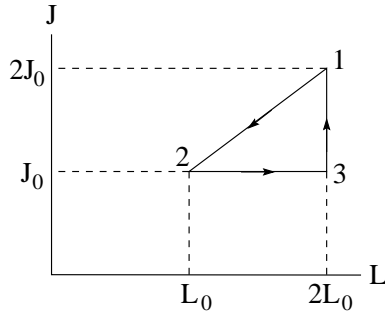
Consider a heat engine that uses a rubber band in the three-step cycle shown. The equation of state $J = \alpha LT$ with $\alpha = \text{const}$ relates the tension J in the band to the length L of the band and to the absolute temperature T . The heat capacity of the band at constant length is $C_L = \text{const}$. Calculate the heat transfer ΔQ and the work performance ΔW in each of the three steps in the cyclic process shown:

1 \rightarrow 2 relaxation at $T = \text{const}$,

2 \rightarrow 3 expansion at $J = \text{const}$,

3 \rightarrow 1 heating up at $L = \text{const}$.

From these results calculate the efficiency η of the rubber band heat engine. Compare η with the efficiency of a Carnot engine operating between the same temperatures.



Solution:

[tex40] Equation of state and adiabat of an elastic band

Experimentally one finds the following response functions of a band of elastic material

$$\left(\frac{\partial J}{\partial L}\right)_T = \frac{aT}{L_0} \left[1 + 2\left(\frac{L_0}{L}\right)^3\right], \quad \left(\frac{\partial J}{\partial T}\right)_L = \frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L}\right)^3\right],$$

where J is the tension, L is the length, T is the temperature, and a, L_0 are constants. The heat capacity at constant length is $C_L = \text{const.}$

- (a) Use this empirical information to reconstruct the equation of state $J(T, L)$.
- (b) Calculate the response function $(\partial L / \partial T)_J$ and discuss its physical meaning.
- (c) If the band is stretched adiabatically from length L_0 at temperature T_0 to length $2L_0$, what is the final temperature?

Solution:

[tex28] Determining C_V of condensed matter

The direct measurement of the heat capacity at constant volume C_V for condensed matter is very difficult. Therefore, express C_V in terms of the following quantities, all of which are experimentally more accessible: the heat capacity at constant pressure C_p , the isothermal compressibility κ_T , the mass density ρ , and the sound velocity $c = \sqrt{(\partial p / \partial \rho)_S}$.

Solution:

[tex23] Thermodynamics of black-body radiation

Electromagnetic radiation inside a cavity is in thermal equilibrium with the walls at temperature T . The radiation has an energy density that depends only on the temperature, i.e. its internal energy has the form $U(T, V) = Ve(T)$. The radiation pressure is determined by the energy density alone: $p = \frac{1}{3}e(T)$. (a) Use the consistency equations for the total differential dS to show that the energy density has the form $e(T) = \sigma T^4$, where σ is a constant, now known as the *Stefan-Boltzmann constant*. In this argument, the additional assumption enters that $e(T) \rightarrow 0$ for $T \rightarrow 0$. (b) Determine the entropy $S(T, V)$ and the thermodynamic potentials $U(S, V)$, $E(S, p)$, $A(T, V)$, $G(T, p)$. (c) Determine the isotherms and adiabates in the (V, p) -plane. (d) Determine the response functions $C_V, C_p, \kappa_T, \kappa_S, \alpha_p$.

Solution:

[tex24] Carnot cycle of thermal radiation

Describe the four steps of a Carnot engine, where the operating material is black-body radiation. The internal energy is given by Stefan's law, $U(T, V) = \sigma T^4 V$. The equation of state is $p = \frac{1}{3} \sigma T^4$. Determine the work performance ΔW and the heat transfer ΔQ during each of the four steps and derive the Carnot efficiency from these results. Sketch the cycle in the (V, p) -plane.

Solution: